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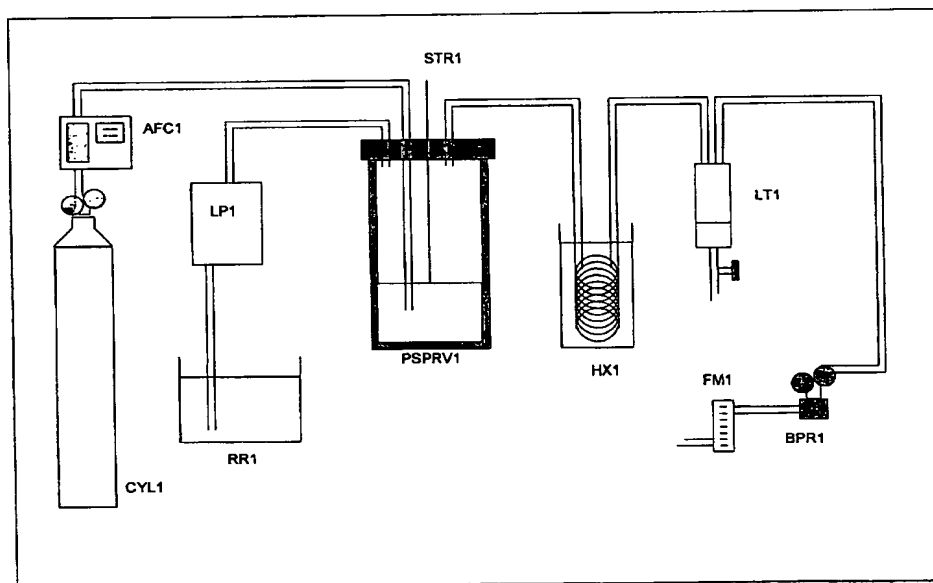
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(54) Title: IMPROVEMENTS IN OR RELATING TO WET OXIDATION



(57) Abstract: An oxidation process is described which involves subjecting a feedstock which contains oxidisable material to temperature, pressure and contact with an oxidant. Excess water and volatile oxidation products, such as carbon dioxide, formic acid and acetic acid, are removed in the vapour phase. A catalyst may be employed to increase the rate of reaction. Preferred catalysts include the transition metal ions. Advantageously, the process may be operated in a continuous manner wherein the feedstock is continuously introduced into a reactor and a vapour phase containing volatile oxidation products continuously removed. The process is particularly applicable to the treatment of consumer and industrial waste.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

IMPROVEMENTS IN OR RELATING TO WET OXIDATION

TECHNICAL FIELD

5 The present invention relates to wet oxidation. A process is provided, in which organic or inorganic oxidisable material is subjected to an aqueous phase oxidation process to give oxidation products which are substantially in the vapour phase. Advantageously, the process is suitable for continuous operation. The process is particularly useful for the treatment of industrial waste.

10

BACKGROUND ART

Wet oxidation is an effective method for lowering the chemical oxygen demand (COD) of many compounds. When applied to waste treatment processes, wet oxidation involves
15 the aqueous phase oxidation of predominantly organic compounds at elevated temperatures and pressures. Temperatures of 127–300°C and pressures of 0.5–20 MPa are generally employed [1].

The vast majority of known processes relate to the wet oxidation of municipal sewage
20 sludge [1].

The known processes all operate using the same general principles. A liquid or slurry is introduced into an autoclave *via* a pumping mechanism, and reacted with an oxidant under pressures and temperatures in the regions noted above. The products of the
25 reaction are then removed from the reactor, largely in the liquid phase, cooled, and separated outside of the reactor.

Oxygen is only sparingly soluble in water and its use as an oxidant requires the process to be operated at a pressure significantly above that of the vapour pressure of the liquid at
30 the operating temperature, in order to minimise the loss of liquid inside the reactor. However, the use of high temperatures and pressures which necessitate the use of, for

example: expensive alloys in the fabrication of reactors; costly valves; and significant safety measures; together with the long reaction times required, have limited the application of wet oxidation.

- 5 One approach which has been applied to overcome these obstacles is the use of an appropriate catalyst. If a catalyst is employed to increase the rate of reaction, a lower temperature, and correspondingly lower pressure, is generally required. Typical catalysts comprise transition metal ions, the most effective of which are generally copper, manganese and iron. Due to their toxicity to other forms of life, these ions are restricted
- 10 in terms of their disposal into public waterways. Therefore, strict disposal regulations apply to catalysts such as those based on transition metals.

Accordingly, the treated product from a wet oxidation reactor must have the concentration of the catalyst reduced to levels that satisfy the regulatory requirements.

- 15 This may be achieved by, for example: precipitation as the hydroxide; pH modification to allow removal as the oxide; or a range of osmotic and electrochemical methods. All are costly and may be difficult to operate, thus limiting the use of catalysts in known processes.

- 20 Moreover, a mixture of compounds will usually be present in the waste stream to be treated and this further limits the known processes. The individual compounds generally have different rates of reaction, and therefore require different reactor residence times either in batchwise or continuous processes. This means that either:

- (a) the reactor residence time is limited to that of the compound within the mixture
- 25 with the slowest rate of reaction, which generally dictates the use of a proportionally larger reactor; or
- (b) the process is less efficient and achieves a lower reduction in, for example, COD, biological oxygen demand (BOD) and percent conversion.

- 30 In addition, the more stable compounds—which are correspondingly more difficult to oxidise—may remain in the output stream from the reactor, and it is these compounds which are more likely to have detrimental environmental consequences.

These disadvantages have hindered the development of wet oxidation as a method for treating waste. Accordingly, it is an object of the present invention to provide a wet oxidation process which goes some way to overcoming these limitations, or at least provides the public with a useful choice.

5

SUMMARY OF INVENTION

In a first aspect, the present invention provides a process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:

- 10 (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
- (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
- 15 (c) separating said vapour phase from said fluid phase.

20

The non-volatile oxidisable material may be a single substance or a mixture of substances, and may be a waste product such as industrial waste, consumer waste or a component thereof, all of which are well known in the art.

Generally the oxidisable material comprises an organic substance.

Preferably, the oxidisable material comprises one or more components selected from the group consisting of: lipids; proteins; carbohydrates (for example starch or cellulose);
25 mineral oils; vegetable oils; waxes; and hydrocarbons.

Optionally, the oxidisable material includes one or more oxidisable inorganic compounds.

Oxidants which may be used in a process of the invention include, but are not limited to
30 air, oxygen, ozone, peroxide, and mixtures thereof. Preferably, the oxidant is air, oxygen or peroxide.

The temperature at which the process is operated is generally between about 100°C and about 350°C and the pressure between 0.7 and 17.2 MPa.

Preferably, the temperature at which the process is operated is between about 190°C and about 300°C, more preferably between about 190°C and about 280°C. In two particularly preferred embodiments, the temperature is between about 190°C and about 210°C or between about 220°C and about 240°C.

Preferably, the pressure at which the process is operated is between about 1.4 MPa and about 13.0 MPa, more preferably between about 2.0 MPa and about 3.5 MPa. In two particularly preferred embodiments, the pressure is between about 2.1 MPa and about 2.9 MPa or between about 2.9 MPa and about 3.4 MPa.

The process of the invention is particularly applicable to the treatment of industrial and consumer waste.

Optionally, a catalyst may be employed to increase the rate of reaction. Suitable catalysts include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II) ions, iron (II) ions or manganese (II) ions, or a mixture thereof.

More preferably, the catalyst is copper (II) ions.

Desirably, oxidation is carried out as a continuous process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed from the reactor.

The oxidation products in the separated vapour phase may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present invention provides an oxidation product when produced by a process of the invention.

In a preferred embodiment, the oxidation product is acetic acid, formic acid, carbon dioxide or a mixture thereof.

In another aspect, the present invention provides a non-volatile salt when produced by an oxidation process of the invention.

5 Although the present invention is broadly as defined above, those persons skilled in the art will appreciate that the invention is not limited thereto and that the invention also includes embodiments of which the following description gives examples.

DESCRIPTION OF THE DRAWINGS

10 Figure 1 is a schematic diagram of apparatus particularly suitable for performing an oxidation process of the invention on a laboratory scale.

Figure 2 is a schematic diagram of the additional modifications which may be made to the apparatus of Figure 1 to facilitate the treatment of slurries.

15

Figure 3 is a schematic diagram of a proposed pilot plant or commercial plant design.

Figure 4 is a graph of COD and temperature vs time for the oxidation of glucose at 200°C in a process of the invention.

20

Figure 5 is a graph of pH and temperature vs time for oxidation of glucose at 200°C in a process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

25

The present invention is broadly directed to the oxidation of various substances, conveniently described herein as "Phase Transfer Wet Oxidation".

30

Accordingly, in a first aspect, the present invention provides a process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:

- (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
- (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
- 5 (c) separating said vapour phase from said fluid phase.

The term "feedstock" as used herein includes, but is not limited to, aqueous liquids, solutions, suspensions, colloids, emulsions, and other mixtures. The term may also include slurries formed from substantially dry material to which is added a suitable
10 aqueous liquid.

The amount of oxidisable material in the feedstock is typically less than about 10% by weight.

- 15 In one embodiment, the feedstock is fed directly into the apparatus. In an alternative embodiment, water is firstly introduced into the apparatus and then the oxidisable material is introduced into the apparatus.

The term "contact" as used herein generally means admixing the aqueous solution or
20 slurry with the oxidant in a suitable apparatus, hereinafter referred to as the "reactor", which is of a type designed to withstand the temperature and pressure and is well known in the art. Suitable reactors include, but are not limited to autoclaves and pressure reactors.

- 25 The term "non-volatile" as used herein means that the oxidisable material is largely in the solid or liquid state under the temperature and pressure conditions in the reactor.

It will be appreciated that, preferably, the reactor is one in which the interfacial area between the oxidant and the feedstock is maximised, and from which the reaction
30 products and the volatile non-oxidisable components present in the feedstock (for example, water) may be readily removed in the vapour phase.

The term "separate" as used herein generally means removing the vapour phase from the reactor while excluding the fluid phase.

5 In one embodiment, phase separation may be achieved by keeping the reaction pressure near to the vapour pressure of water at the reaction temperature by, for example, rapidly lowering the pressure of the reactor to remove volumes of treated material by flash vaporisation at specific intervals.

10 The feedstock may be introduced into the reactor by means of a pump or hydraulic plunger or by other means as are known in the art. Optionally, the apparatus may incorporate a means of stirring the contents, if and when required.

15 It will be appreciated that the temperature and pressure at which the process of the invention is operated are selected according to the stability or ease of oxidation of the feedstock. The temperature at which the process is operated is generally between about 100°C and 350°C and the pressure between about 0.7 MPa and about 17.2 MPa.

20 Preferably, the temperature at which the process is operated is between about 190°C and about 300°C, more preferably between about 190°C and about 280°C. In two particularly preferred embodiments, the temperature is between about 190°C and about 210°C or between about 220°C and about 240°C.

25 Preferably, the pressure at which the process is operated is between about 1.4 MPa and about 13.0 MPa, more preferably between about 2.0 MPa and about 3.5 MPa. In two particularly preferred embodiments, the pressure is between about 2.1 MPa and about 2.9 MPa or between about 2.9 MPa and about 3.4 MPa.

30 The present invention also contemplates processes in which the feedstock is at the desired temperature and/or pressure prior to entering the reactor, for example a process in which the feedstock comprises a mixture of non-volatile oxidisable material and superheated steam.

Oxidants which may be used in a process of the invention include, but are not limited to: air, oxygen, ozone, peroxide, and mixtures thereof. Preferably, the oxidant is air, oxygen or peroxide. The oxidant is introduced into the reactor at an equivalent or greater pressure to that of the reactor and at a rate sufficient to effect oxidation.

5

Substances amenable to oxidation by a process of the invention are those which are relatively non-volatile under the temperature and pressure conditions at which the process is operated, and for which the major oxidation products are volatile under the same or similar conditions.

10

The feedstock may comprise more than one non-volatile oxidisable material. The non-volatile oxidisable material may be a single substance or a mixture of substances, and may be a waste product such as industrial waste, consumer waste or a component thereof, all of which are well known in the art.

15

Generally the oxidisable material comprises an organic substance.

20

Preferably, the oxidisable material comprises one or more components selected from the group consisting of: lipids; proteins; carbohydrates (for example starch or cellulose); mineral oils; vegetable oils; waxes; and hydrocarbons.

25

It will be appreciated that some inorganic substances may be oxidised in a process of the invention. For example, phosphorus may be oxidised to phosphate in a process of the invention. Similarly, sulfur may be oxidised to sulfate and nitrogen to nitrate. Therefore, the oxidisable material may optionally include one or more oxidisable inorganic compounds.

30

As explained in detail below, the process of the invention is particularly applicable to the treatment of industrial and consumer waste. That is the invention provides a process for treating waste, the process comprising combining the waste with water, if required, then subjecting the waste to steps (a) to (c) as detailed above.

The term "treat" as used herein means that the chemical oxygen demand (COD) or biological oxygen demand (BOD) of the waste is reduced.

- Suitable waste for treatment in a process of the invention includes consumer and industrial waste including, but not limited to:
- 5 dairy shed waste, for example "cow dung" from milking shed wash downs;
 - pig and chicken waste;
 - milk processing plant waste including milk, cheese and butter vat wash downs;
 - food processing wastes, for example from the washing and preparation of vegetables;
 - 10 waste from the wine industry and brewing industry;
 - food waste;
 - shipboard waste;
 - waste in environmentally sensitive locations;
 - waste from the wash downs and oil-traps of petroleum service stations and garages;
 - 15 waste fats and proteins from the meat processing industry, for example abattoir stickwater;
 - wool-scouring waste;
 - sewage;
 - medical waste;
 - 20 fibre, ink and polymeric material from the deinking waste produced in the recycling of paper;
 - waste paper and paper products;
 - waste from the wood processing industry including waste wood and wood products, wood fibre, saw dust and wood treated with preservatives;
 - 25 rubber waste;
 - plastic waste; and
 - tannin and colorants from wood pulping streams.

- Similarly, other waste treatment applications to which a process of the invention may be applied include, but are not limited to:
- 30 reclamation of sites contaminated by organic materials including at least petrochemical, gas works, timber treatment or agrochemical sites; and
 - recovery of inorganic preservatives from wood.

While the oxidisable substances are relatively non-volatile, their primary wet oxidation products are generally much more volatile compounds such as carbon dioxide, acetic acid, and formic acid. It will therefore be understood that while the feedstock is introduced to the reactor in the liquid or solid phase, the products of the oxidation reaction may be removed from the reactor in the vapour phase, hence the name "Phase Transfer Wet Oxidation".

Accordingly, a significant portion of the oxidation products from a process of the invention is removed in the gas phase. This is in contrast to the known processes in which the reaction products are generally removed in the liquid phase.

It will be appreciated that any compound which is volatile at the reaction temperature may be present in the gas phase. However, any higher molecular weight compounds, such as higher organic acids, will generally be present at very low concentrations.

The oxidation products in the separated vapour phase may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present invention provides an oxidation product when produced by an oxidation process of the invention.

Typical oxidation products include, but are not limited to, carbon dioxide, formic acid, acetic acid, higher organic acids and mixtures thereof.

In a preferred embodiment, the oxidation product is acetic acid, formic acid, carbon dioxide or a mixture thereof.

More preferably, the oxidation product is acetic acid or a mixture of acetic acid and formic acid. The acetic acid so provided is sterile. Accordingly, the acetic acid may be converted to acetate and utilised as a nutrient source for micro-organisms.

Advantageously, the temperature and pressure of the vapour phase is reduced in a heat exchanger and the heat recycled to the incoming feedstock. In another embodiment, the

incoming feedstock and the reactor contents are optionally heated by the addition of external heat.

Desirably, oxidation may be carried out as a continuous process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed.

When the oxidation is carried out as a continuous process the reactor will advantageously incorporate a means of measuring the fluid level within the reactor, such that the reactor does not run dry.

10

If a mixture of oxidisable substances is subjected to a process of the invention, then those with a faster rate of reaction will oxidise first, and the products of the reaction are removed in the vapour phase as they are formed. More stable substances, with a correspondingly slower rate of reaction, will remain in the reactor until they have oxidised to volatile products. Any water in the feedstock entering the reactor will also be vaporised, thereby permitting more feedstock to enter the reactor. This is in contrast to the known processes, which require either a large reactor, or provide a reduction in the percent conversion of oxidisable substances to their oxidation products.

Optionally, a catalyst may be employed to increase the rate of reaction. Suitable catalysts include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II) ions, iron (II) ions or manganese (II) ions, or a mixture thereof. More preferably, the catalyst is copper (II) ions.

While it will be appreciated that the process of the invention is amenable to heterogeneous catalysis, the catalyst may advantageously be in the form of a homogenous catalyst. In the known processes, the use of homogenous catalysts generally leads to catalyst leaching and subsequent contamination of the downstream products. However, it will be appreciated that, in a process of the present invention, the catalyst may remain in the dissolved liquid phase in the reactor. In this way an initial amount of catalyst may be introduced into the reactor, where it will remain while multiple volumes of feedstock are introduced into the reactor and the oxidation products removed in the vapour phase.

Thus, the catalyst does not need to be replaced until the entire reactor is emptied, for example for cleaning, or unless a feedstock with a high salt content is being treated. For feedstocks with a high salt content, the non-volatile salts accumulate inside the reactor, which may require a "flush" cycle as the solubility limit of the least-soluble salt is approached and the effective reactor volume decreases.

Desirably, any useful non-volatile salts which accumulate in the reactor may be recovered. In one embodiment, applying a process of the invention to the treatment of tannalised wood waste will lead to an accumulation of copper chrome arsenate in the reactor which may be recovered and recycled. In an alternative embodiment, phosphate, sulfate and nitrate salts resulting from the oxidation of proteins in a process of the invention will accumulate in the reactor and may precipitate when their saturation solubility is exceeded. Advantageously, the concentrated solution or precipitated salts may be used for other applications, for example as a fertiliser.

Accordingly, in another aspect, the present invention provides a non-volatile salt when produced by an oxidation process of the invention.

Those persons skilled in the art will appreciate that there is a relationship between the internal volume of the reactor and the volume of feedstock that may be treated by means of Phase Transfer Wet Oxidation before the system is flushed and the process restarted. This ratio may be conveniently referred to as the "Batch Ratio".

It will be appreciated that unless external heat is applied, the heat-balance of the overall reaction must be great enough to compensate for the enthalpy of vaporisation at the reactor operating temperature, along with the energy required to bring the feedstock to that temperature. Heat will be provided by the exothermic nature of the reaction and may also be recovered, *via* a cool-down heat exchanger, from the vapour phase as it is removed from the reactor. This is summarised in Equation 1.

EQUATION 1

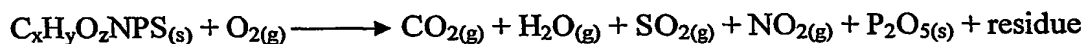
$$Q = \Delta H_{\text{rxt}} + E_{\text{recyc}} - E_{\text{temp}} - m_f \Delta H_v = \Delta H_{\text{rxt}} + E_{\text{recyc}} - m_v c \Delta T - m_f \Delta H_v \geq 0$$

where ΔH_{rxn} is the enthalpy of reaction, E_{recyc} the energy recovered from the cool-down heat exchanger, E_{temp} the energy required to raise the feedstock to the desired operating temperature, ΔH_v the heat of vaporisation of the liquid at the operating temperature, m_f the mass of feedstock, m_v the mass of the vapour, c the specific heat of the feedstock, and ΔT the difference between the feedstock and operating temperatures.

The pollution potential for a waste stream is often measured in terms of its COD which equates to the mass of oxygen required to convert the sample from its original “high energy state” to carbon dioxide and water. A similar measurement provides the BOD which equates to the mass of oxygen consumed by a standard biological organism—generally a species of bacteria—as it uses the waste stream as a nutrient source. Thus, an effective measure of the extent to which a sample has been degraded, and one which is often used as a legal means of classification into “acceptable” and “unacceptable” waste streams, is the difference between the COD and/or BOD of the sample before and after processing.

For thermal combustion at atmospheric pressure, where the oxidant is in the gas phase, the reactants are converted to, *inter alia*, carbon dioxide, water, sulfur dioxide, nitrogen dioxide, phosphorus pentoxide and sulfur dioxide (Equation 2).

EQUATION 2



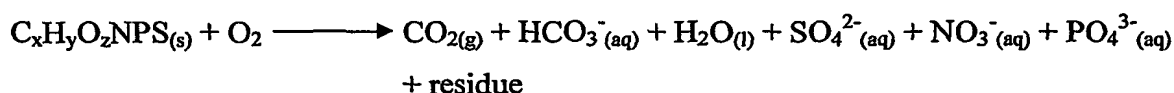
While often utilised in the past as a disposal method, thermal combustion has lost favour due to venting of the gases produced to the atmosphere. In addition, the reactants must be sufficiently dry to allow the combustion to be self-sustaining.

In contrast to thermal combustion, wet oxidation utilises dissolved oxygen at elevated pressures and temperatures to carry out the oxidation. However, the products of the oxidation of nitrogen, phosphorus and sulfur, for example, are kept in the liquid phase with sulfur as sulfate, nitrogen as nitrate and phosphorus as phosphate (Equation 3). A

portion of the carbon is oxidised to carbon dioxide and dissolves in the liquid phase to form carbonate/bicarbonate ions.

EQUATION 3

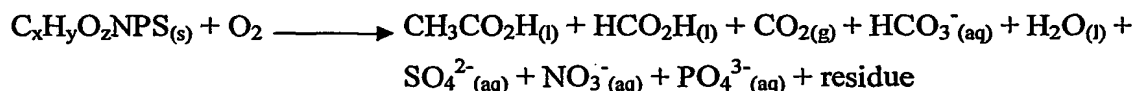
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Thus, the theoretical products of wet oxidation are carbonate/bicarbonate and water, plus any inorganic ions, generally oxy-anions, resulting from the presence of other elements in the oxidisable material. However, in practice the reaction does not convert the entire initial carbon loading to carbonate/bicarbonate. Instead, quantities of acetic and formic acids are formed (Equation 4) and much lower levels of higher molecular weight organic acids.

15

EQUATION 4



20

These acids are generally the major products of reaction, and thus the primary source of COD and BOD in the products.

An analysis of the phase diagram of acetic acid in water at the temperatures and pressures associated with wet oxidation, shows that the concentrations of this compound in the vapour phase and the liquid phase are almost identical. These data are presented in Table 1, Table 2 and Table 3. Formic acid behaves in a similar manner. Therefore, as the oxidisable substances are non-volatile under the conditions generally used for wet oxidation and the products of the reaction—principally acetic acid, formic acid, water and carbon dioxide—are volatile under these conditions, the two may be separated.

30

TABLE 1 Acetic acid concentrations (10% w/w in water initially) in the vapour phase ¹

<i>Temp. (°C)</i>	<i>Pressure (kPa)</i>	<i>Acetic acid (%w/w)</i>
160	551	5.0
180	965	7.4
200	1516	8.0
220	1964	8.2
240	3032	8.1
260	4272	8.1
280	5684	8.2
300	7441	8.8

5 **TABLE 2** Acetic acid concentrations (20 % w/w in water initially) in the vapour phase ¹

<i>Temp. (°C)</i>	<i>Pressure (kPa)</i>	<i>Acetic acid (%w/w)</i>
160	655	14.1
180	1034	17.5
200	1516	17.3
220	1998	18.9
240	3032	17.5
260	4237	18.0
280	5753	18.5
300	7441	18.0

10 **TABLE 3** Acetic acid concentrations (40 % w/w in water initially) in the vapour phase ¹

<i>Temp. (°C)</i>	<i>Pressure (kPa)</i>	<i>Acetic acid (%w/w)²</i>
160	620	29.8
180	896	32.6
200	1550	33.0
220	2101	36.1
240	3032	37.3
260	3858	37.6
280	5581	39.0
300 ³	6787	43.2

¹1 L samples in the 2 L autoclave. For the 20 & 40% w/w runs, the samples were purged with argon for 10 minutes prior to heating. ²Estimated by integration of the ¹H NMR exchangeable and non-exchangeable peaks. ³Liquid removed after run was a dark-brown colour, indicating possible decomposition and carbonisation of the initial acid.

This contrasts with the known processes, wherein both the *untreated* waste stream (the feedstock) and the *treated* stream (the products) are generally in the liquid phase.

EXPERIMENTAL

5

EXAMPLE 1

Glucose

- 10 Glucose is similar to the constituents of many industrial waste streams, in particular cellulose and starch. In addition, glucose is readily oxidisable, and the products of reaction easily analysed. Therefore it is an ideal model compound.

Method

15

- The apparatus shown in, and described with reference to, Figure 1 was used for this Example. A 1% (w/v) solution of glucose was pumped from the reactant reservoir RR1 by an HPLC pump LP1 at a rate of 8 mL.min⁻¹ into an autoclave PSPRV1 (a Parr Stirred Pressure Reactor Vessel of 2 L capacity, of which less than 400 mL was used at any one
20 time), the autoclave having been pre-filled with 300 mL of the aforesaid glucose solution. Air was introduced from a standard gas cylinder CYL1 through an air flow controller AFC1 at a rate of approximately 15 standard cubic feet per hour (SCFH), measured on the outlet line from the reactor. This is significantly more than that required to effect the oxidation of the glucose solution, but was deemed necessary due to the poor mixing
25 observed in the small reactor. The reactor was stirred by means of a motor-driven rod STR1 with stirring blades submerged below the liquid level, and rotated at a rate of 600 rpm.

- The reactor was heated electrically to a temperature of 200°C, and the temperature kept at
30 this level by means of a thermostat-led control system.

The outlet port was connected to a cooling bath HX1 and liquid trap LT1, whereby the reaction products could be removed as required. The pressure and flow of gas through the outlet port was controlled *via* a back-pressure regulator BPR1 coupled to a pressure gauge. Carbon dioxide, nitrogen, and unreacted oxidant passed through this regulator, the pressure dropped to ambient, and the gas flow on the outlet side was measured by gas flow meter FM1 before the gases were vented to the atmosphere.

A summary of the reaction conditions used in this Example are listed in Table 4.

10 **TABLE 4 Summary of Conditions Used in the Treatment of Glucose**

<i>Component</i>	<i>Value</i>	<i>Units</i>
Pressure at tank (regulator)	2.76	MPa
Pressure in reactor	2.62	MPa
Back pressure regulator	2.21	MPa
Reaction temperature	200	°C
Pumping rate (feedstock)	8.00	mL.min ⁻¹
Stirring speed	600	rpm
Oxidant flow	15	SCFH (air)
Reactor volume (total)	2000	mL
Reactor volume (utilised)	300	mL

Results

15 The chemical oxygen demand (COD), pH, and low molecular weight organic acids produced were analysed. These are listed in Table 5, Table 6 and Table 7. The results show that the process was able to be operated with the feedstock (glucose solution) being continuously added to the reactor, and the products of reaction (primarily acetic acid, formic acid and carbon dioxide) being continuously withdrawn from the reactor in the vapour phase, before being condensed to ambient temperature.

The COD of both the feedstock (glucose) and the products (primarily water, acetic and formic acids) were measured throughout the experiment and the results are presented in Table 6. The feedstock COD (COD_i) was constant at 10.3 g.L⁻¹, while the COD of the treated stream (COD_f) varied between 0.65 and 2.23 g.L⁻¹. The change in temperature

and in the COD of the treated stream with respect to time is represented graphically in Figure 4.

A total of 6.40 g COD (as glucose) was added to the reactor. The product stream had a total COD of 1.56 g which is a reduction of 75.6 % from that of the untreated glucose (see Table 7). The pH of the treated stream withdrawn in the vapour phase was measured and these data are presented in Table 5. The pH of the treated stream decreased to approximately 3, consistent with the formation of the low molecular weight organic acids. The change in temperature and in the pH of the treated stream withdrawn in the vapour phase with respect to time is represented graphically in Figure 5.

TABLE 5 Low Molecular Weight Organic Acids Produced in the Oxidation of Glucose at 200°C

<i>Min</i>	<i>Acetic (mg.L⁻¹)</i>	<i>Formic (mg.L⁻¹)</i>	<i>pH</i>
0	0	0	7.30
31	42	196	3.72
40	316	107	3.14
65	586	224	2.91
93	486	2129	2.85
120	340	1030	2.86
180	308	1162	2.90
Post run	511	5755	2.64

TABLE 6 Reduction of COD in the Oxidation of Glucose

<i>Min</i>	<i>°C</i>	<i>V_{out}</i> <i>(mL/min)</i>	<i>COD_i</i> <i>(g/L)</i>	<i>COD_f</i> <i>(g/L)</i>	<i>Red (%)</i> <i>in COD</i>
0	25	0.0	10.34	-	-
10	60	0.0	-	-	-
28	193	0.0	-	-	-
31	200	16.5	10.34	0.65	93.8
40	195	8.5	10.34	1.53	85.2
65	198	7.0	10.34	2.03	80.4
93	190	4.0	10.34	2.23	78.4
120	204	4.4	10.34	2.11	79.6
180	203	1.5	10.34	2.23	78.4
Post run	-	102.9	10.34	3.51	66.1

Table 6 also shows the volume of product removed at each stage in the reaction which was typically $7 \text{ mL} \cdot \text{min}^{-1}$, though a large variation was noted due to the equipment used. It is unlikely that such a variation would exist in a scaled-up process.

5 **TABLE 7 Summary of the Oxidation of Glucose**

<i>Component</i>	<i>Result</i>
Total COD in	6.40 g
Total COD out	1.56 g
Reduction in COD	4.84 g
Percentage reduction in COD	75.6 % w/w

EXAMPLE 2

10 **Lard ($100 \text{ mg} \cdot \text{kg}^{-1} \text{ Cu}^{2+}$)**

Commercial lard is similar to the constituents of many waste streams from the dairy and meat processing industries. It is not readily oxidisable under ambient conditions, and generally requires a catalyst to achieve a significant reduction in chemical oxygen
15 demand at temperatures below 270°C . Standard batch runs were carried out with an equivalent sample (stickwater from a local abattoir) both with and without a catalyst to illustrate this. It was found that *without* a catalyst, a temperature of 280°C was required to achieve a reduction in COD of 78 %. At 230°C , a catalyst concentration of $100 \text{ mg} \cdot \text{kg}^{-1} \text{ Cu}^{2+}$ gave a reduction in COD of 69 %, while at a concentration of
20 $1000 \text{ mg} \cdot \text{kg}^{-1} \text{ Cu}^{2+}$ (see Example 3) a reduction in COD of 83 % was achieved. However, when *no* catalyst was used at the same temperature (230°C), the reduction in COD was limited to approximately 55 %.

Method

25

The experimental apparatus shown in Figure 1 and described above, with the modification shown in, and described with reference to, Figure 2 was used for this Example.

An emulsion of lard in water (approximately 1% w/v) RS1 was loaded into a hydraulic plunger together with some large ball bearings BB1 to provide mixing when the hydraulic plunger was agitated by shaking. An HPLC pump LP2 was used to pump water from reservoir WR1 into the hydraulic plunger *via* line HPL1 through the bolt-on endplate EP1. The water slowly filled the hydraulic plunger, moving the piston MP1 and pumping the emulsion at a rate of 8 mL/min through inlet RI1 into an autoclave PSPRV1 (2 L capacity, of which less than 400 mL was used at any one time), the autoclave having been pre-filled with 300 mL of water containing $100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$ (as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

- 10 Pumping of the emulsion was not started until the reactor had reached operating temperature (230°C) after which it was kept at this level by means of a thermostat controlled system. Air was introduced into the autoclave through inlet RI2 from a standard gas cylinder at a rate of approximately 11 ± 2 standard cubic feet per hour (SCFH), measured on the outlet line from the reactor. This is significantly more than that required to effect the oxidation of the lard solution, but was deemed necessary due to the poor mixing observed in the small reactor. The reactor was stirred by means of a motor-driven rod STR1 with stirring blades submerged below the liquid level, and rotated at a rate of 600 rpm.
- 20 The outlet port RO1 was connected to a cooling bath and liquid trap, whereby the reaction products could be removed as required. The pressure and flow of gas through the outlet port was controlled *via* a back-pressure regulator coupled to a pressure gauge. Carbon dioxide, nitrogen, and unreacted oxidant passed through this regulator, the pressure dropped to ambient, and the gas flow on the outlet side measured before venting the gases to atmosphere.

A summary of the reaction conditions used in this Example are listed in Table 8.

TABLE 8 Summary of Conditions Used in the Oxidation of Commercial Lard with 100 mg.kg⁻¹ Cu²⁺

<i>Component</i>	<i>Value</i>	<i>Units</i>
Pressure at tank (regulator)	3.31	MPa
Pressure in reactor	3.17	MPa
Back pressure regulator	3.03	MPa
Reaction temperature	230	°C
Pumping rate (feedstock) ¹	8.00	mL.min ⁻¹
Stirring speed	600	rpm
Oxidant flow	11 ± 2	SCFH (air)
Reactor volume (total)	2000	mL
Reactor volume (utilised)	300	mL

5 ¹Pumping not started until time = 51 min (when operating temperature was reached).

Results

10 The results of the phase-transfer wet oxidation of commercial lard with 100 mg.kg⁻¹ Cu²⁺ are shown in Table 9, Table 10, Table 11 and Table 12.

15 The results show that a sample of lard (as an emulsion in water) could be continuously pumped into the reactor, while at the same time the products of reaction could be continuously removed in the vapour phase and cooled in a heat-exchanger before exiting the system. Further to this, an initial dose of catalyst at a concentration of 100 mg.kg⁻¹ could treat the entire sample, and provide a reduction in COD greater than that able to be achieved in the absence of a catalyst. It should also be noted that while 100 mg.kg⁻¹ of catalyst was used, if this is recalculated over the entire treated volume, it then equates to 22.5 mg.kg⁻¹.

20

The COD of both the untreated and treated streams were measured throughout the course of the reaction and the results are presented in Table 10. The (untreated) emulsion of lard in water had a constant COD of 5476 mg.kg⁻¹, while the treated products had a COD in the order of approximately 1000 mg.kg⁻¹. In total, the feedstock had a total COD of 25 5.65 g, while the treated stream had a total COD of 1.99 g which is a reduction of 64.7 % (see Table 12).

TABLE 9 Oxidation of Lard ($100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$)—pH, Temperature and Condensate Volumes

<i>Time (min)</i>	<i>Temp (°C)</i>	<i>V_{out} (mL)</i>	<i>pH</i>
0 ¹	18		8.70
60	225	170.0	6.67
70	227	100.1	4.60
80	235	50.5	3.70
90	223	39.4	3.58
100	227	39.6	3.50
120	227	92.4	3.62
150	225	116.3	3.18
180	227	176.4	2.84
<i>Vol left in reactor:</i>		154.0	2.46

5 ¹ Sample taken from inlet line to reactor

TABLE 10 Oxidation of Lard ($100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$)—COD data

<i>Time (min)</i>	<i>COD (mg.L⁻¹)</i>
Untreated	5476
60	2600
120	634
180	970
Post run	4214

10 **TABLE 11** Oxidation of Lard ($100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$)—Formic and Acetic acid Concentrations

<i>Time (min)</i>	<i>Acetic (mg.L⁻¹)</i>	<i>Formic (mg.L⁻¹)</i>
Pre-run	32	50
60	80	63
70	62	70
80	68	80
90	85	91
100	100	90
120	99	82
150	101	89
180	120	116
Post-run	216	211

15 As shown in Table 9, the pH of the treated stream dropped from 6.67 to 2.84 during the course of reaction which is consistent with the formation of formic and acetic acids. The

concentration of these acids was also measured during the course of the reaction and the results are presented in Table 11. The concentration was found to be in the order of 70 mg.kg⁻¹ for both acetic and formic acid.

5 **TABLE 12 Summary of Results in the Oxidation of Lard (100 mg.kg⁻¹ Cu²⁺)**

<i>Component</i>	<i>Result</i>
Total COD in	5.65 g
Total COD out	1.99 g
Reduction in COD	3.66 g
Percentage reduction in COD	64.7 % w/w
Total volume treated	1332 mL
Lost as vapour	393 mL
Batch ratio	> 4.4 (based on 300 mL)

EXAMPLE 3

10 Lard (1000 mg.kg⁻¹ Cu²⁺)

Method

The method used was identical to that for Example 2 (Lard (100 mg.kg⁻¹ Cu²⁺)) except that 1000 mg.kg⁻¹ Cu²⁺ was used as the catalyst. As with Example 2, the experimental apparatus used was that shown in Figure 1 and Figure 2.

TABLE 13 Summary of Conditions Used in the Oxidation of Commercial Lard with 1000 mg.kg⁻¹ Cu²⁺

<i>Component</i>	<i>Value</i>	<i>Units</i>
Pressure at tank (regulator)	3.24	MPa
Pressure in reactor	3.17	MPa
Back pressure regulator	3.03	MPa
Reaction temperature	230	°C
Pumping rate (feedstock) ¹	8.00	mL.min ⁻¹
Stirring speed	600	rpm
Oxidant flow	8	SCFH (air)
Reactor volume (total)	2000	mL
Reactor volume (utilised)	300	mL

¹Pumping not started until operating temperature was reached (denoted t=0).

A summary of the reaction conditions used in this Example are listed in Table 13.

Results

- 5 The results are presented in Table 14, Table 15 and Table 16. These show that when the initial dose of catalyst is increased to 1000 mg.kg^{-1} a reduction in COD of 83 % may be achieved, with the same concentration of catalyst treating approximately 5.8 volumes of waste. It should be noted that the volume treated was limited only by the equipment available, in particular the size of the hydraulic plunger used to transfer the feedstock into the autoclave. In practice the volume able to be treated by a single dose of catalyst would be many times greater than that achieved here.

Samples were withdrawn at periodic intervals from the treated stream and their COD and volume measured. The sample volumes are shown in Table 14 and the COD in Table 15.

- 15 The volume of the treated stream was slightly less than that pumped in, due to the partial loss of carbon dioxide as vapour from the reaction. Additionally, the oxidant used was dry air from a compressed cylinder, which upon leaving the reaction would have taken up a small volume of water.

20 **TABLE 14** Oxidation of Lard¹ at 230°C with $1000 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$

<i>Time (min)</i>	<i>Temp (°C)</i>	<i>V_{out} (mL)</i>
0	sample taken from inlet line to reactor ²	
10	225	86.3
20	225	77.2
30	227	55.8
45	227	105.9
60	225	101.1
90	225	227.8
120	225	200.0
150	227	227.3
180	227	216.6
Vol left in reactor:		154.0

- 25 ¹300 mL H₂O initially in the reactor, with 1.20 g CuSO₄.5H₂O ($1000 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$). Reactor brought to 230°C before pumping from the hydraulic plunger began. ²i.e. this equates to the untreated sample.

The COD of the feedstock was constant at 6850 mg.kg⁻¹ while that of the treated products was found to be approximately 1400 mg.kg⁻¹.

Overall, the feedstock had a total COD of 9.90 g, while the products recovered had total
5 COD of 1.68 g which is a reduction of 83 % (see Table 16).

TABLE 15 Oxidation of Lard (1000 mg.kg⁻¹ Cu²⁺)—COD data

<i>Time (min)</i>	<i>COD (mg.L⁻¹)</i>
0	6850
10	1190
20	1190
30	1190
45	1400
60	1400
90	1480
120	1250
150	1220
180	1220
Post-run	2020

10 **TABLE 16 Summary of Results in the Oxidation of Lard (1000 mg.kg⁻¹ Cu²⁺)**

<i>Component</i>	<i>Result</i>
Total COD in	9.90g
Total COD out	1.68 g
Reduction in COD	8.19 g
Percentage reduction in COD	83.0 % w/w
Total volume treated	1740 mL
Lost as vapour	288 mL
Batch ratio	5.8 (based on 300 mL)

EXAMPLE 4

15 A proposed pilot plant or commercial plant design utilising the process of the invention is schematically shown in, and described with reference to, Figure 3.

Non-volatile oxidisable material held in a reservoir FR1 would be combined with sufficient water from inlet WI1 to form the feedstock which is transferred into a reactor
20 vessel by pump LP3. The temperature of the feedstock would be increased by heat

exchanger HX2 which may recycle the heat recovered from the oxidation products removed in the vapour phase by cool-down heat exchanger HX3. It will be appreciated that the feedstock need be heated only to make up the heat balance of the reaction.

- 5 An oxidant would be introduced into the reactor vessel through inlet GI1. Contact between the oxidant and the fluid phase will then be promoted by means of a stirrer STR2 which mixes the reactor contents. The fluid level within the reactor may be monitored by a system of level sensors LS1 connected to a suitable process control system.
- 10 The temperature of the fluid phase in the reactor would be controlled by a heating unit and heat exchanger HX4 by means of the recirculating loop RL1 and pump LP4. HX4 may also recycle the heat recovered from the oxidation products removed in the vapour phase by cool-down heat exchanger HX3
- 15 The vapour phase products of the oxidation reaction would be separated from the fluid phase and removed from the reactor through cool-down heat exchanger HX3. The temperature and pressure of the product stream is thereby reduced. The resultant product stream would pass into liquid trap LT2 where gas phase reaction products such as carbon dioxide may be recovered from the mix of uncondensed gases at outlet GO1 while liquid
- 20 phase reaction products such as water, formic acid and acetic acid may be recovered at outlet LO1.

- The reactor could be emptied, when required, through outlet LO2 and the heat from the reactor contents may be recovered by heat exchanger HX5. Accordingly, useful non-
- 25 volatile salts which accumulate in the reactor may be recovered and any catalyst used may be recycled or subject to suitable disposal.

INDUSTRIAL APPLICATION

- 30 It will be appreciated that, in use, the present invention provides a process for oxidising a feedstock which may be applied to the treatment of industrial waste. Advantageously, the reactor may be of a significantly smaller volume than that used in known processes due to the removal of both water and volatile oxidation products from the reactor in the vapour

phase, allowing for further feedstock to enter the system. In this way the process may be operated in a continuous manner.

5 In addition, a homogenous catalyst may be used in the treatment of more stable compounds, and the catalyst retained in the reactor while multiple volumes of waste were treated. A variety of consumer and industrial waste is amenable to treatment by a process of the invention, and these are discussed above.

10 Furthermore, the present invention also provides a sterile source of, for example, acetic acid which may be utilised, following conversion to acetate, as a nutrient source for micro-organisms.

15 Those persons skilled in the art will further appreciate that the present description is provided by way of example only and that the scope of the invention is not limited thereto.

REFERENCES

- 20 1. Kolackowski, S., Plucinski, P., Beltran, F., Rivas, F., McLurgh, D. "Wet air oxidation: a review of process technologies and aspects in reactor design", *Chem. Eng. J. (Lausanne)*, 1999, 73, 2, 143-160.

CLAIMS

1. A process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:
 - 5 (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
 - (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
 - (c) separating said vapour phase from said fluid phase.
- 10 2. A process as claimed in claim 1 wherein the feedstock is an aqueous liquid, solution, suspension, colloid, emulsion or other mixture.
3. A process as claimed in claim 1 or 2 wherein the feedstock comprises a slurry
15 formed from substantially dry material to which is added an aqueous liquid.
4. A process as claimed in any one of claims 1 to 3 wherein the oxidisable material comprises less than about 10% by weight of the feedstock.
- 20 5. A process as claimed in any one of claims 1 to 4 wherein the oxidisable material comprises a mixture of substances.
6. A process as claimed in any one of claims 1 to 5 wherein the oxidisable material is a waste product.
- 25 7. A process as claimed in claim 6 wherein the waste product is industrial waste, consumer waste or a component thereof.
8. A process as claimed in claim 6 or claim 7 wherein the oxidisable material is
30 waste selected from the group consisting of: dairy shed waste; pig and chicken waste; milk processing plant waste; milk, cheese and butter vat wash downs; food processing waste; waste from the wine industry and brewing industry; food waste; shipboard waste; waste in environmentally sensitive locations; waste from the

wash downs and oil-traps of petroleum service stations and garages; waste fats and proteins from the meat processing industry; wool-scouring waste; sewage; medical waste; fibre, ink and polymeric material from the deinking waste produced in the recycling of paper; waste paper and paper products; waste from the wood processing industry including waste wood and wood products, wood fibre, saw dust and wood treated with preservatives; rubber waste; plastic waste; and tannin and colorants from wood pulping streams.

5

10

9. A process as claimed in any one of claims 1 to 8 wherein the process is applied to the reclamation of sites contaminated by organic materials.

10. A process as claimed in claim 9 wherein said site is selected from the group consisting of: petrochemical works; gas works; timber treatment sites; and agrochemical sites.

15

11. A process as claimed in any one of claims 1 to 7 wherein the oxidisable material comprises an organic substance.

20

12. A process as claimed in claim 11 wherein the organic substance is selected from the group consisting of: lipids; proteins; carbohydrates; mineral oils; vegetable oils; waxes; and hydrocarbons.

25

13. A process as claimed in claim 12 wherein the organic substance is a carbohydrate selected from starch and cellulose.

30

14. A process as claimed in any one of claims 1 to 13 wherein the oxidisable material includes one or more oxidisable inorganic compounds.

15. A process as claimed in any one of claims 1 to 14 wherein the oxidant is selected from the group consisting of: air; oxygen; ozone; peroxide; and mixtures thereof.

16. A process as claimed in claim 15 wherein the oxidant is selected from the group consisting of: air; oxygen; and peroxide.

17. A process as claimed in any one of claims 1 to 16 wherein the temperature is between about 100°C and about 350°C.
- 5 18. A process as claimed in any one of claims 1 to 17 wherein the temperature is between about 190°C and about 300°C.
19. A process as claimed in any one of claims 1 to 18 wherein the temperature is between about 190°C and about 280°C.
- 10 20. A process as claimed in any one of claims 1 to 19 wherein the temperature is between about 190°C and about 210°C.
21. A process as claimed in any one of claims 1 to 19 wherein the temperature is between about 220°C and about 240°C.
- 15 22. A process as claimed in any one of claims 1 to 20 wherein the pressure is between about 0.7 MPa and about 17.2 MPa.
23. A process as claimed in any one of claims 1 to 22 wherein the pressure is between about 1.4 MPa and about 13.0 MPa.
- 20 24. A process as claimed in any one of claims 1 to 23 wherein the pressure is between about 2.0 MPa and about 3.5 MPa.
- 25 25. A process as claimed in any one of claims 1 to 24 wherein the pressure is between about 2.1 MPa and about 2.9 MPa.
26. A process as claimed in any one of claims 1 to 24 wherein the pressure is between about 2.9 MPa and about 3.4 MPa.
- 30 27. A process as claimed in any one of claims 1 to 25 wherein the feedstock of (a) is contacted with the oxidant in the presence of a catalyst.

28. A process as claimed in claim 27 wherein the catalyst is a homogenous catalyst.
29. A process as claimed in claim 27 or claim 28 wherein the catalyst is selected from the group consisting of the transition metal ions and mixtures thereof.
- 5 30. A process as claimed in any one of claims 27 to 29 wherein the catalyst is selected from the group consisting of: copper (II) ions; iron (II) ions; manganese (II) ions; and mixtures thereof.
- 10 31. A process as claimed in any one of claims 27 to 30 wherein the catalyst is copper (II) ions.
32. A process as claimed in any one of claims 1 to 31 wherein oxidation is carried out as a continuous process wherein the feedstock is continuously introduced into a reactor and the vapour phase continuously removed from the reactor.
- 15 33. A process as claimed in any one of claims 1 to 32 wherein the vapour phase is separated from the fluid phase by flash vaporisation.
- 20 34. A process as claimed in any one of claims 1 to 33 further including the step of reducing the temperature and pressure of the vapour phase to recover at least one oxidation product.
- 25 35. A process as claimed in claim 34 wherein the oxidation product is selected from the group consisting of: carbon dioxide; formic acid; acetic acid; higher organic acids; and mixtures thereof.
- 30 36. A process as claimed in claim 34 or claim 35 wherein the oxidation product is selected from the group consisting of: acetic acid; formic acid; carbon dioxide and mixtures thereof.
37. An oxidation product when produced by a process as claimed in any one of claims 34 to 36.

38. A process as claimed in any one of claims 1 to 36 further comprising the step of recovering at least one non-volatile salt from the fluid phase.
39. A process as claimed in claim 38 wherein the non-volatile salt is recovered as a concentrated solution or a precipitate.
40. A process as claimed in claim 38 or claim 39 wherein the non-volatile salt is an inorganic wood preservative.
41. A non-volatile salt when produced by a process as claimed in any one of claims 38 to 40.

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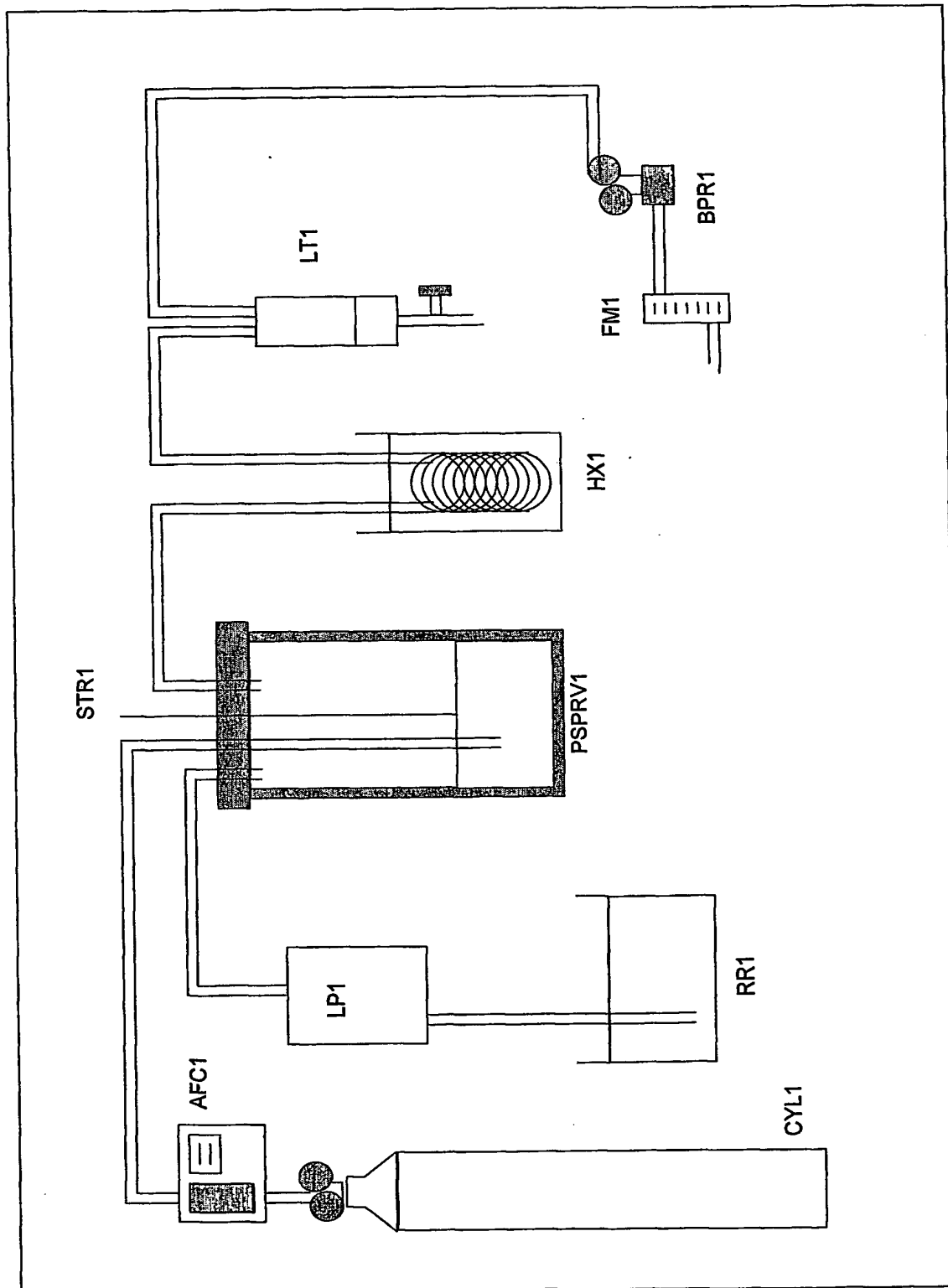


FIGURE 1

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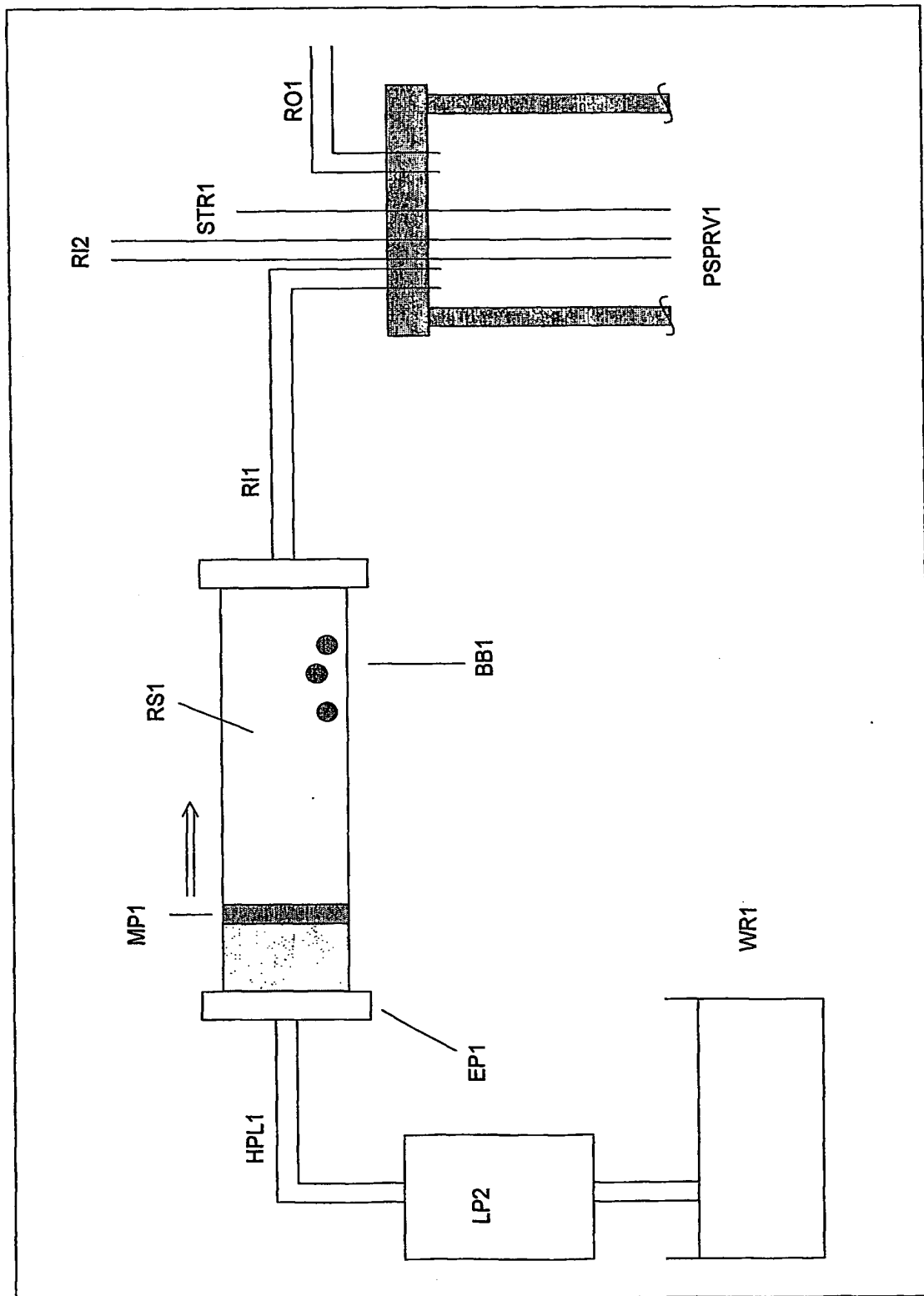


FIGURE 2

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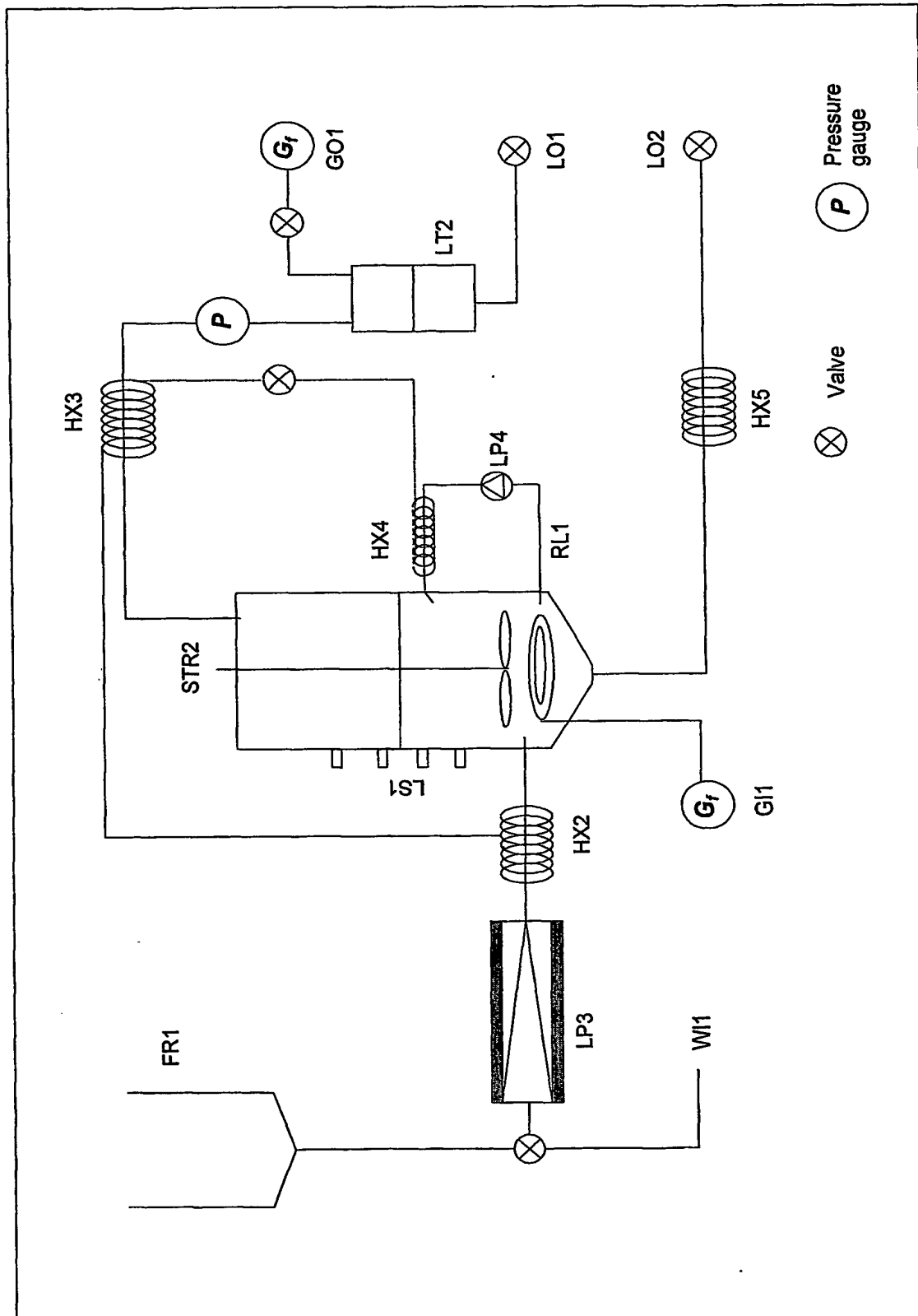


FIGURE 3

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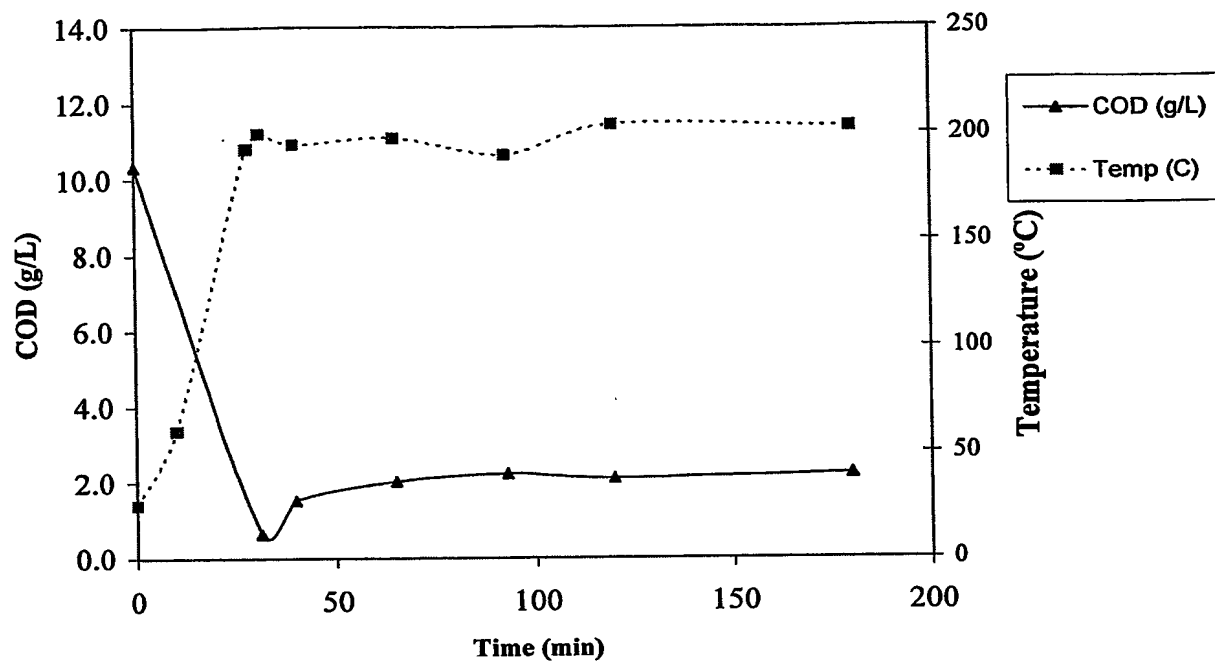


FIGURE 4

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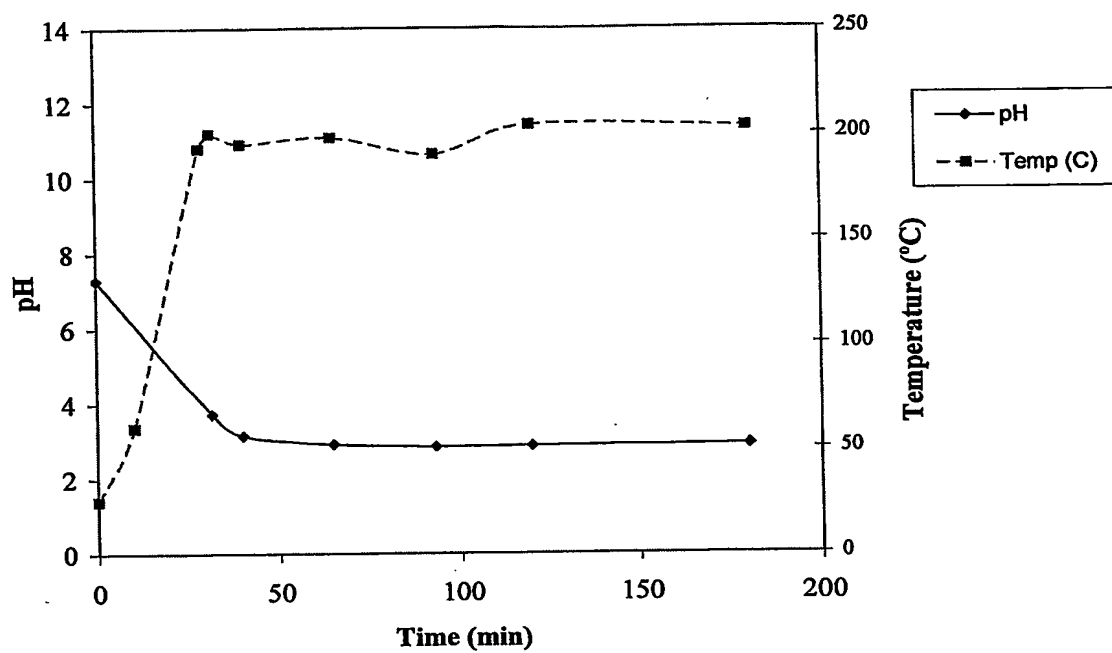


FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ03/00128

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : A62D 3/00; C02F 1/72, 1/74, 1/78, 1/04; C07B 33/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI: wet oxidation		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2,249,945 A (UNITED STATES FILTER CORPORATION) 1 April 2000 Whole document	1-41
X	EP 431 932 B (NIPPON SHOKUBAI CO., LTD) 12 June 1991 Whole document	1-41
X	EP 560 505 A (ZIMPRO PASSAVANT ENVIRONMENTAL SYSTEMS, INC.) 15 September 1993 Whole document	1-41
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 27 August 2003		Date of mailing of the international search report - 2 SEP 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer GAYE HOROBIN Telephone No : (02) 6283 2069

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ03/00128

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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EP	560505	IN	178648	JP	5337477	US	5262060
US	5240619	CA	2095803	EP	610616	MX	9304013
US	6190564	NONE					
WO	9705073	AU	66497/96	CN	1192194	US	5651897
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WO	9736663	AU	25987/97				
WO	8806144	AU	13676/88	DK	5715/88	EP	284754
		US	5053142	US	5370801	CA	19931116
AU	67711/90	JP	3224692	JP	4118095		

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